

SHORT COMMUNICATIONS

Radiation Chemistry

Low-Temperature Liquid-Phase Radiation-Induced Oxidation of Hexafluoropropylene with Molecular Oxygen: Effect of Reaction Conditions on the Structure of Perfluoropolyether Polyperoxide

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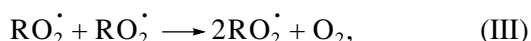
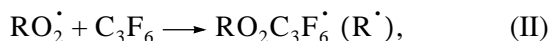
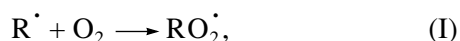
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The formation and development of innovative technologies required the production of liquid polymers that possess a set of unique properties for operation under severe physicochemical conditions. The main requirements imposed on these polymers, which are designed for use as heat-transfer agents, dielectric materials, pressure fluids, oils, lubricants, etc., are high chemical and thermal stability, insolubility in commonly used organic solvents, low glass-transition temperatures, incombustibility, good lubricating properties, low volatility, weak dependence of the viscosity on temperature, and nontoxicity.

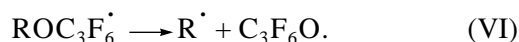
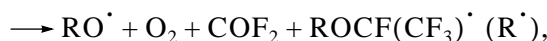
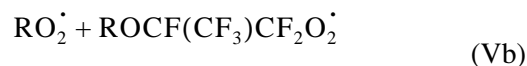
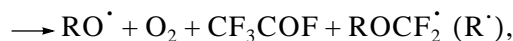
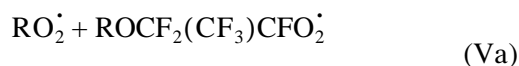
Perfluorinated oxygen-containing polymers of the second generation, namely, perfluoropolyethers, fully conform to the above requirements. The low-temperature liquid-phase oxidation of perfluoroolefins by molecular oxygen is the most important process for the synthesis of perfluoropolyethers, in which the oxidation of hexafluoropropylene currently occupies a prominent place [1].

Perfluoropolyether polyperoxide (PFPP), the liquid oligomer with a molecular mass of the order 10^2 – 10^4 , is the major reaction product. The $-\text{C}_3\text{F}_6\text{O}-$, $-\text{CF}_2\text{O}-$, and $-\text{CF}(\text{CF}_3)\text{O}-$ ether units predominate in the structure of PFPP [2]. Peroxy units account for no more than 10% of the total units. The mechanism of PFPP formation is the following [2, 3]:



Low-molecular-weight compounds are also formed, namely, trifluoroacetyl fluoride (CF_3COF), carbonyl fluoride (COF_2), and hexafluoropropylene oxide

($\text{C}_3\text{F}_6\text{O}$). The following elementary steps are responsible for these compounds [4, 5]:



The structure, that is, the ratio between units with different numbers of carbon atoms, is the most important characteristic of PFPP. Because the mechanism of this reaction was studied in sufficient detail, we have a unique opportunity to calculate the contents of different units of the oligomer from data on the rates of consumption of hexafluoropropylene and of formation of low-molecular-weight products without measuring NMR spectra. Indeed, reaction (V) is responsible for the formation of units with the number of carbon atoms equal to 1 and 2. At the same time, reaction (VI) decreases the number of three-carbon units. Thus, the amounts of units of different structures can be calculated by the following equations:

$$N_{-\text{CF}_2-} = \frac{W_{\text{CF}_3\text{COF}}}{W_{\text{C}_3\text{F}_6} - W_{\text{C}_3\text{F}_6\text{O}}} \times 100 (\%),$$

$$N_{-\text{CF}(\text{CF}_3)-} = \frac{W_{\text{COF}_2}}{W_{\text{C}_3\text{F}_6} - W_{\text{C}_3\text{F}_6\text{O}}} \times 100 (\%),$$

$$N_{-\text{C}_3\text{F}_6-} = 100 - N_{-\text{CF}_2-} - N_{-\text{CF}(\text{CF}_3)-} (\%),$$

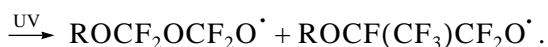
where $W_{\text{C}_3\text{F}_6}$, $W_{\text{CF}_3\text{COF}}$, W_{COF_2} , and $W_{\text{C}_3\text{F}_6\text{O}}$ are the rates of consumption of hexafluoropropylene and of formation of trifluoroacetyl fluoride, carbonyl fluoride, and hexafluoropropylene oxide, respectively ($\text{mol l}^{-1} \text{ s}^{-1}$).

Table 1. Concentrations of $-\text{CF}_2-$ units in the PFPP structure, %

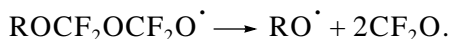
P_{O_2} , MPa	Temperature, K						
	303	288	273	258	243	228	213
0.10	—	51	28	15	7	4	2
0.29	60	37	16	13	—	—	—
0.49	51	34	13	11	8	—	—
0.64	48	—	—	—	—	—	—
0.78	45	—	—	—	—	—	—
0.98	42	35	16	17	10	11	—
1.47	38	37	14	14	—	—	—
1.96	38	38	14	—	—	—	—

Values for the above rates were repeatedly published. The most complete data were given in [6]. The experimental procedure was described, for example, in [7]. Tables 1 and 2 summarize the calculated values of $N_{-\text{CF}_2-}$ and $N_{-\text{CF}(\text{CF}_3)-}$ at various oxygen pressures for the reaction of PFPP synthesis initiated by ^{60}Co γ -radiation with a dose rate of 0.9 Gy/s.

Note that such calculations can be performed only for the initiation of the reaction with γ -radiation because UV radiation, which can also be applied to initiate this reaction, selectively decomposes the peroxy units of PFPP as follows:



Next,



Thus, the degradation of peroxy units can disturb the one to one ratio between molecules of a low-molecular-weight acid fluoride and units with the number of carbon atoms lower than that in the parent olefin. As can be seen in Tables 1 and 2, the proportions of $-\text{CF}_2-$ and $-\text{CF}(\text{CF}_3)-$ units in the structure of PFPP increase with increasing the synthesis temperature. This is due to the fact that the activation energy at the steps of formation of low-molecular-weight acid fluorides is

Table 2. Concentrations of $-\text{CF}(\text{CF}_3)-$ units in the PFPP structure, %

P_{O_2} , MPa	Temperature, K						
	303	288	273	258	243	228	213
0.10	—	39	18	10	6	4	3
0.29	40	24	11	10	—	—	—
0.49	34	21	10	8	7	—	—
0.64	34	—	—	—	—	—	—
0.78	30	—	—	—	—	—	—
0.98	28	26	11	14	8	10	—
1.47	26	24	10	9	—	—	—
1.96	28	26	12	—	—	—	—

higher than the apparent activation energy of the overall process [6]. It can also be seen that, at 273–303 K, the proportion of these units decreases with increasing oxygen pressure. The reason is that, as the pressure of oxygen increases, reaction (VI), which removes $-\text{C}_3\text{F}_6\text{O}-$ units from the PFPP structure, becomes increasingly suppressed by competing reaction (II). At lower temperatures, the $\text{C}_3\text{F}_6\text{O}$ formation rate is insignificant and has almost no effect on the oligomer structure.

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